

**PAPERMAKING FURNISH COMPRISING SOLVENTLESS**  
**CATIONIC POLYMER RETENTION AID COMBINED WITH**  
**PHENOLIC RESIN AND POLYETHYLENE OXIDE**

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**FIELD OF THE INVENTION**

This invention relates to papermaking. More particularly, it relates to a papermaking furnish that comprises a solventless cationic polymer retention aid in combination with phenolic resin and polyethylene oxide (PEO) to increase retention and/or drainage in the furnish.

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**BACKGROUND OF THE INVENTION**

In the manufacture of paper, an aqueous suspension of cellulosic fibers, optionally containing a filler and cationic starch, as well as other papermaking chemicals, is spread over a wire or cloth and water is removed therefrom to form a fiber web or sheet. Such aqueous suspension or slurry is called "papermaking furnish". The removal of water or dewatering of the furnish as well as retention of fines, fillers and other papermaking chemicals in the paper sheet are very important to the efficient recovery and production rate and to the cost of manufacture of the paper and its quality.

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It is well known to use a combination of phenolic resin and polyethylene oxide as a flocculent to improve retention and drainage in the production of paper and paperboard, particularly in newsprint applications where mechanical pulp containing dissolved organic contaminants causes some detrimental effects. In such systems, the phenolic resin is usually added first to the furnish, before the last shear point, such as a fan pump, and PEO is added second, usually near the headbox of the paper machine, in order to

minimize shear. As is known, shearing is provided by one or more of the cleaning, mixing and pumping stages in the papermaking process and the shear breaks down the flocks formed by the high molecular weight polymer into microflocs, which are further agglomerated, for instance with the help of cationic starch.

5           It has been suggested that the mechanism of the phenolic resin/PEO two-component retention system consists firstly of adsorption of the phenolic resin onto fibers and fines, followed by attachment of PEO to the phenolic hydroxyl groups of the resin, forming high molecular weight polymeric networks which serve to retain the fines and also promote drainage. Examples of such two-component retention system are disclosed,  
10           for instance, in U.S. Patents Nos. 4,070,236 and 5,472,570.

          The phenolic resin/PEO two-component system has the advantage of being independent of most dissolved and colloidal contaminants in the water circuit because it functions by a hydrogen-bonding mechanism. In contrast, cationic polyacrylamides, which are also commonly used as retention aids, are adversely affected by dissolved and  
15           colloidal contaminants found in mechanical pulp.

          In addition, the phenolic resin/PEO two-component system has several other advantages over cationic polyamides, including more favorable effects on the final sheet formation and a better pitch control, which refers to its ability to fix organic contaminants in the paper sheet rather than allowing them to deposit on the mill fabrics and machinery,  
20           thereby causing eventual shutdowns.

          Nevertheless, despite the above advantages, the phenolic resin/PEO retention and drainage system has not been adopted in mills producing grades such as highly filled specialty mechanical paper, fine paper (where mechanical pulp from softwood does not

form a large part of the furnish), and tissue and packaging papers. In these areas, cationic polyacrylamides are the predominant treatment.

The main reason for the lack of success of the phenolic resin/PEO system in the above areas is the reduced performance owing to the lack of organic contaminants in these furnishes compared to the softwood mechanical pulp used in many newsprint applications. These contaminants provide a part of the network mechanism by which this retention system functions and their absence in other furnishes such as sulphate pulp and recycled and deinked pulp has led to the predominance of other retention systems, especially cationic polyacrylamides. In addition it has been found that residual silicate in the pulp from some bleaching and de-inking operations sometimes has an adverse effect on polyethylene oxide causing a loss of retention or drainage. (c.f. Rahman and Tay Tappi Proceedings, 1986 Papermakers Conference, p 189-198).

There is thus a need for an improved phenolic resin/PEO based retention system that would alleviate the above mentioned disadvantages and increase retention and drainage, particularly in furnishes such as sulphide pulp and recycled and de-inked pulp.

#### OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a papermaking furnish with increased retention rate and drainage based on the phenolic resin/PEO retention system.

A further object is to provide a method of increasing retention rate and drainage in a papermaking furnish while also maintaining good sheet quality at reduced cost.

A still further object is to provide a papermaking furnish based on the phenolic resin/PEO retention system which would be suitable for producing highly filled specialty mechanical paper, fine paper and tissue and packaging papers.

Other objects and advantages will become apparent from the following description of the invention.

The applicants have surprisingly discovered that a retention aid consisting of a solventless cationic polymer, which is in the form of an oil-free, water-soluble polymeric dispersion, combined with phenolic resin, such as phenol formaldehyde resin, provides increased retention rate and drainage as well as other advantages, such as reduced cost, when used in conjunction with polyethylene oxide (PEO). When the solventless, cationic polymer retention aid and phenolic resin are added to the furnish, they form a structure which gives a significantly improved reaction with polyethylene oxide when it is added to the furnish. Retention, namely fiber retention, filler retention, and COD-retention (natural resins and other organic contaminants) and drainage are increased to the extent that the above areas of fine paper, recycle packaging grades and other types of paper production become viable areas when this system is used. Additionally increased filler and fines retention is obtained over that which would be achievable using the PEO and phenolic resin combination alone or using the solventless cationic polymer alone.

The solventless, cationic polymer retention aids suitable for the purposes of the present invention are characterized by the fact that they do not contain any oil-phase. They are liquid, aqueous, solventless dispersions of cationic polymers with typical charge densities of between 20 and 75% mole percent, solids content between 2 and 70%, and viscosities in water at 1% of between 2000 and 20000 mPa sec.

The synthesis of such polymeric dispersions is described, for example, in U.S. Patent No. 5,480,934 where it is also indicated that they can be used as a retention agent in paper production, as a soil improvement agent or as a dispersing agent. However, no

suggestion is made in this patent that they could be employed as a component of the phenolic resin/PEO system, resulting in the above mentioned advantages.

The solventless cationic polymer retention aid and phenolic resin may enter the furnish separately at two different points of addition or together at the same point of addition, i.e. they can be used in sequence or together, and their combination reacts much more favourably with PEO than if either component is used alone. The solventless cationic polymer retention aid and the phenolic resin can be added to the furnish either before or after PEO addition.

Solventless cationic polymers are suitable for the purposes of the present invention regardless of the number, type or concentration of the monomers used to make them and they can be in the form of a liquid or dried to a powder. Examples of such polymers are those marketed by Degussa under trade names Praestaret K-325 and Praestaret K-350 as well as Praestol E-125 and Praestor E-150.

Thus, the present invention provides a papermaking furnish comprising a combination of a solventless cationic polymer retention aid with phenolic resin and polyethylene oxide, as a retention system for retaining fines, fillers and other papermaking chemicals in the paper sheet.

In a preferred application, the amount of the solventless cationic retention aid is 0.05 kg/ton to 10 kg/ton based on the weight of dry fibers; the amount of phenolic resin is 0.05 kg/ton to 10 kg/ton of actual resin in the as-supplied material per ton of dry fibers; and the amount of polyethylene oxide is 5 g/ton to 500 g/ton based on the weight of dry fibers, the "ton" being a metric tonne.

The preferred ratio of solventless cationic polymer retention aid to phenolic resin

is from 200:1 to 1:200; that of phenolic resin to PEO from 100:1 to 1:100 and that of solventless cationic polymer retention aid to PEO is from 1:2000 to 2000:1.

The invention also includes a method of increasing retention rate and drainage in a papermaking furnish by adding to the furnish an effective amount of a solventless cationic polymer retention aid in combination with phenolic resin and polyethylene oxide. The effective amount will depend on the type of pulp being dewatered and on the other additives being used. It can readily be established by trial and error before establishing the appropriate amount for a given furnish. The preferred amounts are those already indicated above.

In a further embodiment of the present invention, it has been found that a further increase in sheet drainage and machine speed are achieved when the solventless cationic polymer retention agent is added last, after the PEO addition and after the last point of shear.

In a still further embodiment of this invention, the filler is pretreated with the solventless cationic polymer retention aid before it is added to the stock. This pretreatment is a preflocculation approach and it results in a better dispersion of the filler throughout the stock, better fines/filler retention and better opacifying properties. The pretreated filler is dosed into the stock before the last point of shear and the PEO is preferably dosed near the head box, thus capturing the filler particles as well as other fines and fibers in an apparent network structure.

In summary, this invention utilizes the synergism between the phenolic resin and the solventless cationic polymer retention aid to enhance the performance with polyethylene oxide and to allow the use of polyethylene oxide and phenolic resin in a

wider range of applications, as well as improving existing newsprint applications.

Furthermore, the synergistic phenolic resin/ solventless cationic polymer retention aid combination gives further beneficial effects if the solventless cationic polymer retention aid is premixed with the filler prior to dosing into the stock and reaction with  
5 polyethylene oxide. These effects have been confirmed with acidic and neutral furnishes and a variety of fillers including kaolin, calcite, bentonite and titanium dioxide.

The practice of this invention enables the benefits of polyethylene oxide to be realized in more papermaking applications than is possible at present. These benefits include a more favourable sheet formation than that produced by polyacrylamide  
10 retention agents, an ability to fix pitch contaminants in the sheet and the generally lower dosage rate than with polyacrylamide systems, leading to potentially lower steam consumption in the driers because of the smaller amount of bound water. Other benefits obtained by the practice of this invention are its favourable reaction with starch, and its ability to provide a superior flocculating pretreatment of the filler in order that the  
15 activated filler be more fully dispersed throughout the stock prior to its capture by the addition of the polyethylene oxide component. The provision of a superior flocculating pretreatment of the filler allows the filler to attain its best opacifying power while at the same time its capture by polyethylene oxide ensures good filler retention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Preferred embodiments of the invention will now be described with reference to the drawings, in which:

Fig. 1 is a schematic representation of an arrangement in which the solventless polymer and the phenolic resin are introduced together into the papermaking furnish;

Fig. 2 is a schematic representation of an arrangement in which the solventless polymer and the phenolic resin are introduced separately from one another into the papermaking furnish;

Fig. 3 is a schematic representation of an arrangement in which the solventless polymer is added last into the papermaking furnish; and

Fig. 4 is a schematic representation of an arrangement in which the filler is pretreated with the solventless polymer.

#### DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described with reference to the appended drawings which illustrate some preferred embodiments thereof and in which the same elements are identified by the same reference numbers.

Thus, Fig. 1 illustrates a schematic arrangement of a papermaking process in which the fan pump 10 forms the last point of shear after which the furnish proceeds to the screen 12 and from the screen to the headbox 14. In this embodiment, the solventless polymer and the phenolic resin are introduced together into the furnish between the fan pump 10 and the screen 12 before the introduction of PEO.

According to the embodiment of Fig. 2, the solventless polymer is added to the furnish in advance of the fan pump 10 and prior to the introduction of the phenolic resin and PEO which are added between the fan pump 10 and the screen 12. The solventless polymer is added here as a fiber pretreatment micropolymer.

In the embodiment of Fig. 3, the solventless polymer is added last after the screen 12 and just in advance of the headbox 14. It acts here as a drainage aid.

Finally, in the embodiment of Fig. 4, the solventless polymer is added as a filler



pretreatment in advance of the fan pump 10. Here, the phenolic resin is also added in advance of the fan pump 10, but after the pretreated filler. PEO is added between the fan pump 10 and the screen 12.

It should be noted that the illustrated arrangements are in no way limitative.

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## EXAMPLES

To test the various features of the present invention described above, the following laboratory test procedures were used.

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For retention without pad formation and turbidity tests a Dynamic drainage jar (DDJ) was used with a baffled cylinder and the speed of the stirrer was set at between 500 and 1000 rpm.

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For retention with pad formation, drainage, and formation tests a Dynamic Drainage Analyzer (DDA) was used. The objective in using the DDA was to be able to come as close to papermaking conditions as possible. The DDA is conceived to measure drainage rates through a forming pad. As a result, the measured retention is higher than that obtained using the dynamic drainage jar (DDJ), where no pad is formed. Since a pad is formed in the experiment, the formation of the formed wet sheet can also be obtained.

- Drainage

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Drainage in the DDA is measured as the time from the start of the run until air starts being sucked through the sheet and it is automatically computed to within one hundredth of a second. The drainage is affected by many factors, for example grammage, vacuum, sample volume, type of stock, temperature, wire, and chemicals. It is usually desirable to use the same furnish consistency as in the mill. However, for furnishes with high freeness and fast drainage it can improve the experimental accuracy if a higher

solids content or larger sample volume is used. The opposite is true of a low freeness furnish.

- Retention

Retention is defined as the amount of fiber retained on the wire compared to the amount of fiber going through. The retention in DDA experiments is inherently higher than on a paper machine. However, it correlates very well with the values found with a Britt jar.

The present invention will be illustrated by the following examples, however, without being restricted thereto.

#### 10 EXAMPLE 1

A 1.06% cellulosic fibre slurry consisting of 50% TMP (thermo mechanical pulp – hydrosulfite bleached), 20% DIP (de-inked pulp) and 30% broke was taken from a newsprint mill. The slurry had a clay filler content of 20%. The pH of the slurry was set at 4.5.

15 For retention and turbidity tests a Dynamic drainage jar (DDJ) was used with a baffled cylinder and the speed of the stirrer was set at 550 rpm. A 500 ml sample was used for testing. FPR indicates the first pass retention.

For drainage, formation, and retention (with pad formation) tests a Dynamic Drainage Analyzer (DDA) was used with a baffled cylinder and the speed of the stirrer was set at 1000 rpm. A 800 ml sample was used for testing. The vacuum was set at 500 mBar.

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Tables 1 and 2 below show the results when conventional phenol formaldehyde resin-polyethylene oxide retention system is compared to phenol formaldehyde resin-polyethylene oxide – solventless cationic polymer flocculant retention system. In the tables the turbidity is indicated in nephelometric turbidity units (ntu).

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TABLE 1. DDJ TESTING

Product	Product	Product	Product	Product	Product	Retention	Turbidity ntu	Normalized Cost
Name	Dose (g/t)	Name	Dosage (g/t)	Name	Dosage (g/t)	(%)		(0 to 100)
Blank	0	0	0	0	0	43.58%	285	0
Solventless Polymer Flocculant added before phenolic resin and PEO								
solventless, cationic polymer retention aid	200	phenolic resin	240	polyethylene oxide	30	45.85%	275	36.4
	400		240		30	46.02%	249	52.3
	600		240		30	46.33%	256.5	68.2
	800		240		30	46.50%	229.5	84.0
	1000		240		30	46.83%	227	100.0
Solventless Polymer Flocculant added after phenolic resin and PEO								
phenolic resin	240	Polyethylene oxide	30	solventless, cationic polymer retention aid	200	45.08%	246.5	36.4
	240		30		400	45.27%	247	52.3
	240		30		600	45.88%	236	68.2
	240		30		800	47.17%	235	84.1
	240		30		1000	47.36%	234.5	100.0
Solventless Polymer Flocculant added between phenolic resin and PEO								
phenolic resin	240	Solventless, cationic polymer retention aid	200	polyethylene oxide	30	45.90%	249.5	36.4
	240		400		30	45.89%	249	52.3
	240		600		30	46.24%	243.5	68.2
	240		800		30	46.30%	229	84.1
	240		1000		30	46.34%	222	100.0
phenolic resin and PEO alone								
solventless, cationic polymer retention aid	0	phenolic resin	240	polyethylene oxide	30	43.95%	242	20.5
	0		480		60	44.07%	240	40.9
	0		720		90	44.23%	235	61.4
	0		960		120	44.55%	231	81.9
Solventless Polymer Flocculant alone								
solventless, cationic polymer retention aid	200	phenolic resin	0	polyethylene oxide	0	42.92%	290	15.9
	400		0		0	43.62%	290	31.8
	600		0		0	44.22%	288	47.7
	800		0		0	45.25%	276	63.6
	1000		0		0	46.62%	275	79.5

TABLE 2. DDA TESTING

Product	Product	Product	Product	Product	Product	Retention	Drainage	Normalized Cost
Name	Dose (g/t)	Name	Dosage (g/t)	Name	Dosage (g/t)	(%)	(sec)	(0 to 100)
Blank	0	0	0	0	0	76.14	57.50	0
Solventless Polymer Flocculant added before Phenolic resin and PEO								
solventless, cationic polymer retention aid	500	phenolic resin	240	polyethylene oxide	30	78.14	66.26	55.8
	500		800		100	78.10	66.40	100
	1000		240		30	78.08	64.14	92.6
Solventless Polymer Flocculant added after Phenolic resin and PEO								
phenolic resin	240	polyethylene oxide	30	solventless, cationic polymer retention aid	500	77.69	58.94	55.8
	480		60		500	78.25	58.97	74.7
	240		30		1000	81.70	59.80	92.6
	800		100		500	83.28	50.32	100.0
Solventless Polymer Flocculant added between Phenolic resin and PEO								
phenolic resin	240	solventless, cationic polymer retention aid	500	polyethylene oxide	30	78.94	63.63	55.8
	240		1000		30	78.95	65.20	92.6
Phenolic resin and PEO alone								
		phenolic resin	240	polyethylene oxide	30	77.86	58.44	19.0
			480		60	80.27	55.47	37.9
			800		100	83.38	49.86	63.2
Solventless Polymer alone								
solventless, cationic polymer retention aid	200	phenolic resin	0	polyethylene oxide	0	76.08	57.76	14.7
	400		0		0	77.32	58.82	29.5
	600		0		0	77.27	55.55	44.2
	800		0		0	77.28	55.88	58.9
	1000		0		0	77.54	58.34	73.6

## 5 EXAMPLE 2

A 0.992% cellulose fibre slurry consisting of 10% Kraft and 90% TMP (thermo mechanical pulp – hydrosulfite bleached) was taken from a specialty newsprint mill. The slurry had a clay filler content of 10%. The pH of the slurry was set at 6.0

10 For drainage, formation, and retention (with pad formation) tests a Dynamic Drainage Analyzer (DDA) was used with a baffled cylinder and the speed of the stirrer was set at 1000 rpm. A 800 ml sample was used for testing. The vacuum was set at 500 mBar.

Table 3 below shows the results when conventional phenol formaldehyde resin-polyethylene oxide retention system is compared to phenol formaldehyde resin-polyethylene oxide – solventless, cationic polymer flocculant retention system.

TABLE 3. DDA TESTING

Product Name	Product Dose (g/t)	Product Name	Product Dosage (g/t)	Product Name	Product Dosage (g/t)	Retention (%)	Drainage (sec)	Normalized Cost (0 to 100)
Blank	0	0	0	0	0	78.87	83.93	0
Solventless Polymer Flocculant added before Phenolic resin and PEO								
Solventless, cationic polymer retention aid	350	phenolic resin	1000	Polyethylene oxide	125	83.99	39.70	83.1
	350		600		150	83.60	37.20	73.2
	475		700		175	83.40	34.70	89.3
Phenolic resin and PEO alone								
		phenolic resin	0	polyethylene oxide	150	81.12	49.60	30.3
			1000		200	82.25	38.20	77.8
			1500		150	83.15	45.30	86.4
			2000		125	80.61	47.70	100.0
Solventless Polymer alone								
Solventless, cationic polymer retention aid	500	phenolic resin	0	polyethylene oxide	0	81.50	35.50	29.2
	1000		0		0	80.88	51.00	58.4

### EXAMPLE 3

A 1.12% cellulose fibre slurry consisting of 5% Kraft, 70% TMP (thermo mechanical pulp – hydrosulfite bleached) and 25% deinked pulp (DIP) was taken from a specialty newsprint mill using recycled fibres. The slurry had a clay filler content of 30%. The pH of the slurry was set at 6.2

For retention and turbidity tests a Dynamic drainage jar (DDJ) was used with a baffled cylinder and the speed of the stirrer was set at 550 rpm. A 500 ml sample was used for testing. FPR refers to the first pass retention and FPAR the first pass ash retention.

Table 4 below shows the results when conventional phenol formaldehyde resin-polyethylene oxide retention system is compared to phenol formaldehyde resin-polyethylene oxide – solventless, cationic polymer flocculant retention system.

TABLE 4. DDJ TESTING

Product Name	Product Dose (g/t)	Product Name	Product Dosage (g/t)	Product Name	Product Dosage (g/t)	FPR/FPAR (%)	Turbidity ntu	Normalized Cost (0 to 100)
Blank	0	0	0	0	0	35.6/45.4	86.1	0
Solventless Polymer Flocculant added before phenolic resin and PEO								
solventless, cationic polymer retention aid	300	phenolic resin	420	polyethylene oxide	60	46.0/58.2	36.2	97.8
Solventless Polymer Flocculant added after phenolic resin and PEO								
phenolic resin	420	polyethylene oxide	60	solventless, cationic polymer retention aid	300	42.2/56.5	34.1	97.8
Solventless Polymer Flocculant added between phenolic resin and PEO								
phenolic resin	420	solventless, cationic polymer retention aid	300	polyethylene oxide	60	45.4/57.9	36.2	97.8
phenolic resin and PEO alone								
solventless, cationic polymer retention aid	0	phenolic resin	0	polyethylene oxide	60	37.1/47.8	35.7	26.2
			420		60	42.9/54.8	40.7	60.1
			700		100	41.3/43.3	42.6	100.0
Solventless Polymer Flocculant alone								
solventless, cationic polymer retention aid	300	phenolic resin	0	polyethylene oxide	0	41.1/43.3	35.2	37.8

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For this same mill, the polymer was tested on the machine. The solventless, cationic flocculant was added before the phenolic resin and PEO (in the thick stock). The table below shows the results when conventional phenol formaldehyde resin-polyethylene oxide retention system is compared to phenol formaldehyde resin-polyethylene oxide – solventless, cationic polymer flocculant retention system. All

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relevant machine parameters and polymer dosages are tabulated below in Table 5.

TABLE 5. MACHINE PARAMETERS – BEFORE AND AFTER ADDITION  
OF THE SOLVENTLESS CATIONIC POLYMER RETENTION AID.

Parameter	Without solventless cationic polymer retention aid	With solventless cationic polymer retention aid
Grade	643.01	643.01
Grammage (g/m <sup>2</sup> )	41	41
Speed ( m/min )	813	855
% De-inked pulp (DIP)	0	0
% Softwood bleached kraft (SBK)	25.2	25
1st section Steam ( kPa)	114	100
2nd section Steam ( kPa)	177	210
3rd section Steam ( kPa)	273	258
Head Box consistency (%)	1.154	1.02
White water consistency (%)	0.686	0.537
First pass retention (%)	40.66	47.1
Head box ash content (%)	14.87	8.43
White water ash content (%)	21.1	13.23
First pass ash retention (%)	12.3	17.44
% of ash in the sheet	3	2.3
% of alphatex clay added to headbox	2.01	1.89
Cationic demand ( me/l )	286	213
Headbox turbidity ( ntu )	121	43
White water turbidity ( ntu )	90	32
Solventless cationic polymer dosage ( g/T )	0	300
Phenolic resin dosage ( g/T )	560	235
Coagulant dosage ( g/T )	210	0
Polyethylene oxide dosage ( g/T )	59	38
Cost Decrease (%)	----	-12.60%

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The saving of 12.60% in the cost of production represents a considerable advantage in papermaking.

The above results clearly indicate that the solventless cationic polymer-phenolic resin-PEO combination is the best system to use based on relative costs. The retention systems using the phenolic resin/PEO in combination with the solventless cationic polymer yield the highest DDJ and DDA fines retention, the lowest turbidities and the best drainage rate – a clear indication of the programs ability to retain fines and colloidal substances. This is especially true for the following addition sequence: solventless cationic polymer/phenolic resin/polyethylene oxide. In contrast the solventless cationic polymer or the phenolic resin/polyethylene oxide system used alone result in lower retentions and/or higher turbidities.

From these results it can be concluded that not only is there a synergy between the phenolic resin/PEO system and the solventless cationic polymer, but also that it is the most cost effective system.

It should be noted that this invention is not limited to the specific embodiments described and exemplified above, but that various modification obvious to those skilled in the art can be made without departing from the invention and the scope of the following claims.